

Graphical Design of Fractionating Columns¹

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THE rational design of column apparatus for separating the components of binary mixtures of volatile, miscible components dates back to Sorel.² He assumed that equilibrium is established between the liquid on each plate and the vapor rising from it, and calculated the enrichment from plate to plate by heat and material balances. Sorel's method, though sound, is tedious when applied analytically. Many writers have simplified or modified Sorel's method, among them being Lewis,³ Leslie,⁴ Peters,⁵ Van Nys,⁶ and Gay,⁷ who have all used analytical methods. Lewis's method is typical of many of them. Lewis assumed that the enrichment per plate was small, wrote a general enrichment equation differentially, integrated it, and so determined the number of plates. The larger the number of plates the more accurate is this method, but for columns of but a few plates the error introduced by assuming continuous for stepwise conditions is appreciable.

In all the procedures mentioned above, perfect functioning of the column, and hence complete equilibrium between the vapor and liquid of each plate, is assumed, and the number of plates so determined is the number of theoretical or perfect plates necessary to effect the desired separation. If an actual column is one of the plate type, the number of theoretical plates is divided by an average plate efficiency to translate it into the number of actual plates. If the column is of the packed type the number of theoretical plates is multiplied by the height of column equivalent to one theoretical plate (H. E. T. P.)⁸ if the height of the column is desired. Both factors are experimentally determined and both vary with the design of the column and with the mixture distilled. Since they have not been accurately determined for all types of columns or for all mixtures, there is little practical value in determining theoretical plates with great precision and a method such as Lewis's offers sufficient accuracy in spite of the approximation inherent in it. However, since the equations used in all methods are linear, they adapt themselves to stepwise graphical manipulations, with consequent simplicity without the assumption of continuity from plate to plate.

Graphical methods have been presented by Ponchon,⁹

Rodebush,¹⁰ and Savarit.¹¹ However, it is felt that the following method is simpler, exhibits its results in a plainer manner than any method, analytical or graphical, so far proposed, and is accurate enough for all practical use.

This paper is to consider the determination of the number of theoretical plates only, and it is assumed throughout that the plate efficiency, or the H. E. T. P., for the type of column and the mixture under consideration is approximately known.

Preliminary Assumptions

For the purpose of initial simplification certain assumptions will be made, which are commonly realized or approached in ordinary practice within the precision of these data. It will be shown later that, if necessary for any particular case, the restrictions so imposed can be removed without greatly increasing the complexity of the method. The assumptions are:

1—The number of mols of vapor ascending the column, and hence the molal overflow except for the change at the feed plate, is constant from plate to plate. Since heat losses from the column can ordinarily be neglected either because of lagging or large ratio of volume to surface, and since the absolute boiling points of the components are not far apart (otherwise separation is easy in any case), Trouton's rule requires constant molal vaporization from plate to plate.³

Note—Trouton's rule states that for normal liquids the molal entropy of vaporization is nearly constant, or $(Mr/T) = \text{constant}$, where M = molecular weight, T = boiling temperature (absolute), and r = latent heat per unit weight.

2—The feed enters the column at a temperature equal to the boiling point of the liquid on the feed plate. The feed is usually preheated very nearly to this temperature by the hot waste.

3—The only condenser is a simple or total condenser, so the composition of the product is the same as that of the vapor from the top plate.

Note—A simple condenser condenses all the vapor fed to it, but removes none of the sensible heat of the condensed liquid.

4—The heat is supplied at the base of the column by means of "closed steam," so the condensing steam does not dilute the waste.

Note—Obviously, open steam can be used only when the less volatile component is water, if the mixture is to remain one of two components only.

Nomenclature

The nomenclature is a modification of that used by Lewis. That part of the apparatus above the feed plate will be referred to as the rectifying column and that part below the feed plate as the exhausting column. All concentrations are expressed as mol fractions of the more volatile component. Liquid compositions are denoted by x , and vapor compositions by y . All quantities pertaining to the exhausting column are distinguished from corresponding quantities pertaining to the

A rapid and accurate graphical method is described for computing the theoretical number of plates required in a column for performing a given separation of a binary mixture. The method consists essentially in drawing, on the same rectangular plot, the equilibrium curve for vapor and liquid compositions and straight lines representing the equations for enrichment from plate to plate, and passing from one to the other in a series of steps. It is shown that the effect of varying feed, product, waste, and overflow, as well as the effect of varying temperature of feed, may be represented by very simple geometrical constructions. The application of the method to some more complicated problems is discussed.

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² *Compt. rend.*, **58**, 1128, 1204, 1317 (1889); **68**, 1213 (1894).

³ *THIS JOURNAL*, **14**, 492 (1922).

⁴ "Motor Fuels," 1923, p. 70. Chemical Catalog Co., New York.

⁵ *THIS JOURNAL*, **15**, 402 (1923).

⁶ *Chem. Met. Eng.*, **28**, 207, 255, 311, 359, 408 (1923).

⁷ *Chimie & industrie*, **3**, 157; **4**, 178, 735 (1920); **6**, 567 (1921); **10**, 811, 1026 (1923).

⁸ Peters, *THIS JOURNAL*, **14**, 476 (1922).

⁹ *Tech. moderne*, **13**, 20, 55 (1921).

¹⁰ *THIS JOURNAL*, **14**, 1036 (1922).

¹¹ *Chimie & industrie*, Special No. 737-56, May, 1923.

rectifying column by a line written over them. The plates are numbered from the top plate of the rectifying column down to the bottom plate of the exhausting column. The feed plate, which is the top plate of the exhausting column, will simply be a plate with a definite number. A "general" plate will be denoted by n , if in the rectifying column, or by \bar{n} if in the exhausting column. Where any quantity is written with a subscript, the subscript refers to the point of origin of that quantity; thus y_n means the composition of the vapor rising from plate n and x_{n+1} represents the composition of the liquid descending from plate $\bar{n} + 1$. Other symbols are:

- P = mols of distillate withdrawn as product in a given time
 x_p = composition of product
 F = mols of mixture fed to the apparatus in a given time
 x_f = composition of feed mixture
 W = mols of waste withdrawn from column in a given time
 x_w = composition of waste
 O = mols overflow from any plate in the rectifying column
 \bar{O} = mols overflow from any plate in the exhausting column
 V = mols of vapor rising from any plate in the rectifying column
 \bar{V} = mols of vapor rising from any plate in the exhausting column
 A, A', B, B' = coefficients in the enrichment equations

In the whole discussion, the basis will be 1 mol of product—i. e., $P = 1$.

Derivation of Equations

The following equations have been developed and published many times.

Figure 1 represents a "perfect column" performing in accordance with the assumption listed above. By means of balances of total material and more volatile component it has been repeatedly shown that, for the rectifying column

$$y_{n+1} = \frac{O}{O+1} x_n + \frac{x_p}{O+1} \quad (1)$$

$$\text{Or, if} \quad A = \frac{O}{O+1} \text{ and } B = \frac{x_p}{O+1} \quad (2)$$

$$\text{then} \quad y_{n+1} = Ax_n + B \quad (3)$$

which, when plotted with y as ordinates versus x as abscissas, is the equation of a straight line having a slope of A and a y -axis intercept of B . This equation will be called the enrichment equation of the rectifying column, or simply the enrichment equation, and the straight line representing it the enrichment line of the rectifying column or the rectifying line.

Consider the entire apparatus below a section drawn between plates $\bar{n} + 1$ and n . By material balances, it can be shown that

$$\bar{x}_n = \frac{\bar{O} - W}{\bar{O}} y_{n+1} + \frac{W}{\bar{O}} x_w \quad (4)$$

When Assumptions 1 and 2 are made, a heat balance shows

$$\bar{V} = V \quad (5)$$

and a material balance around the feed plate (Figure 1) shows that

$$\bar{O} = F + O \quad (6)$$

Also, by a material balance on the entire apparatus

$$F = W + 1 \quad (7)$$

Substituting values for \bar{O} and W from Equations 6 and 7 into Equation 4, there results

$$\bar{x}_n = \frac{O+1}{O+F} y_{n+1} + \frac{F-1}{O+F} x_w \quad (8)$$

$$\text{Let} \quad A' = \frac{O+1}{O+F} \text{ and } B' = \frac{F-1}{O+F} x_w \quad (9)$$

$$\text{Then} \quad \bar{x}_n = A' y_{n+1} + B' \quad (10)$$

which is the equation of another straight line having a slope

of $1/A'$ and an x -axis intercept of B' . This equation will be referred to as the enrichment equation of the exhausting column or the exhausting equation, and its straight line as the enrichment line of the exhausting column or the exhausting line.

Use of Enrichment Lines

For every binary mixture there is a definite relationship between x , the composition of the liquid phase, and y , the composition of the vapor phase in equilibrium with it. This relationship is best exhibited in the form of a rectangular plot of y as ordinates versus x as abscissas. The curve so formed is known as the equilibrium curve, and gives the relation between the composition of the liquid on any plate and that of the vapor rising from the same plate.

The equilibrium curve and Equations 3 and 10 are all that is necessary to calculate analytically the compositions of liquid and vapor pertaining to each plate, and hence the number of theoretical plates, once the composition of feed, waste, and product, and magnitudes of feed and overflow have been chosen.

ANALYTICAL METHOD—Plot the equilibrium curve on an x versus y plot, as in Figure 2. Since the condenser used is a simple one, y_1 , the concentration of the vapor from the top plate, is equal to x_p , the composition of the product, and therefore is known. Accordingly, the value of x_1 , the composition of the liquid on the top plate, can be read directly from the equilibrium curve, since it is represented by the abscissa of the point on the curve which has the ordinate y_1 . The coefficients A and B of Equation 3 are calculated from x_p and O . If the equation is written as

$$y_2 = Ax_1 + B$$

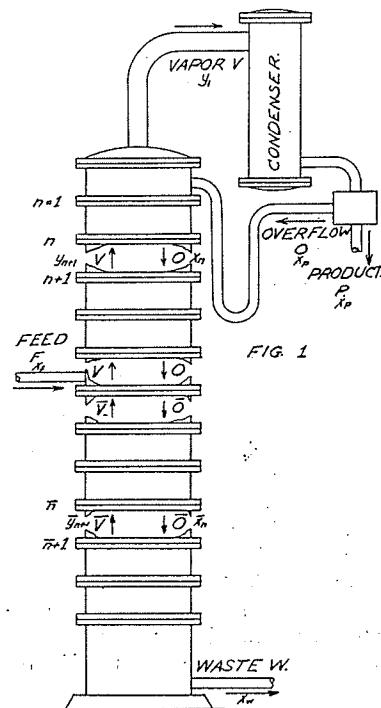
and if the known values of A , B , and x_1 are substituted therein, y_2 , the composition of the vapor rising from plate 2, can be calculated. Since y_2 is determined, x_2 can be read from the equilibrium curve by finding the point thereon with an ordinate y_2 , and reading its abscissa. The value of x_2 is substituted in the equation

$$y_3 = Ax_2 + B$$

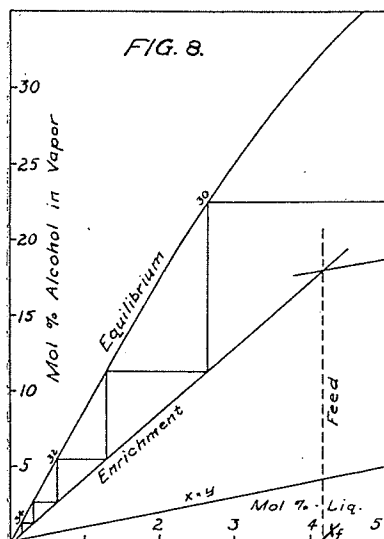
and y_3 calculated. The process is repeated for each plate, and for each plate it is necessary to read one value from the equilibrium curve, and carry out the one calculation by Equation 3. Suppose this process has been carried out for a number

of plates, and $x_1, y_1, x_2, y_2, x_3, y_3$, etc., have been so determined. Suppose the following points are plotted with the coordinates indicated: a , coordinates x_1, y_1 ; b , coordinates x_1, y_2 ; c , (x_2, y_2); d , (x_2, y_3); and e , (x_3, y_3). The points so plotted can be connected by short horizontal and vertical lines, such as ab, bc, cd , and de , since the two points connected by any line have either abscissas or ordinates in common. Furthermore, the points b and d are on a straight line, the equation of which is

$$y = Ax + B$$



and e , respectively, and intersect on the line $x = x_f$. Their slope depends on the overflow only, since F is determined. From Figure 4 it is apparent that, if the lines intersect above the equilibrium curve as at a , the desired separation cannot be effected; if the lines intersect at the intersection of the equilibrium curve and the line $x = x_f$, as at point b , the separation can be attained, but only with an infinite number of perfect plates; and finally, if the lines intersect at any point below the equilibrium curve, as point c , the separation can be effected with a finite number of plates. As the only means of moving the intersection from a to c is by increasing the overflow, by definition the minimum overflow is that overflow for which the rectifying line will intersect the $x = x_f$ line at point b .



The magnitude of the minimum overflow is found by measuring the distance A and computing O from the equation

$$O = \frac{A}{1 - A} \quad (18)$$

which is obtained from Equation 2.

Note—Inspection of Figure 4 shows that for normal mixtures (equilibrium curves concave downward at all points) the largest, or controlling value of the minimum reflux is that corresponding to the composition of the feed.

Infinite Overflow

Inspection of Equations 1 and 8 shows that as O increases indefinitely, the slopes of the enrichment lines approach unity, and for an infinite overflow, the lines coincide with the $x = y$ line, and the minimum number of plates is determined by steps, as in Figure 5.

Constant Boiling Mixtures

Since a constant boiling mixture behaves like a pure component, an infinite number of plates would be necessary to reach the concentration corresponding to such a mixture by distillation alone. The diagram of such a system illustrates this, since if an attempt is made to attain the concentration of the constant boiling mixture, either with the product or the waste, the equilibrium curve, the enrichment line and the $x = y$ line all intersect at the point where x equals the above concentration, and the steps must become infinitely small to reach the apex of the angle in which they are confined.

Technic of Using the Plots

Usually the product is to be nearly pure and the water practically exhausted, speaking in terms of the more volatile component. This means that a single diagram will be too condensed at the ends of the equilibrium curve to use with precision, and separate, enlarged diagrams of these two sectors must be made. Ordinarily, the equilibrium curve will follow Raoult's law at the top and Henry's law at the bottom,¹³

¹³ Walker, Lewis, and McAdams, "Principles of Chemical Engineering," 1923, p. 576. McGraw-Hill Book Company.

and so can be calculated and plotted with any desired precision in these ranges.

As an illustration of the application of the method to an actual case, the example cited by Lewis³ is worked out. An alcohol-water mixture containing 10 per cent alcohol by weight (4.17 mol per cent) is to be separated into a product containing 94.5 per cent alcohol by weight (87.05 mol per cent) and a waste containing not more than 0.1 per cent alcohol by weight (0.039 mol per cent). The overflow in the rectifying column is assumed to be 5 mols per mol of product.

When the equilibrium curve for alcohol-water mixtures is plotted, as in Figure 6, and the values of x_p , x_f , and x_w are plotted thereon, it is evident that the entire operation cannot be indicated on a single diagram of moderate size. Accordingly, three enlarged diagrams are drawn, as in Figures 7, 8, and 9, and used with Figure 6, Figure 7 being an enlargement between the limits $x = 70$ and $x = 90$ mol per cent, and Figures 8 and 9 from $x = 5$ to $x = 0$ mol per cent. The enrichment lines are then drawn, the rectifying line passing through the point P (coordinates x_p, y_1) (Figure 7), and with a slope of $5/(5+1) = 0.833$, and the exhausting line passing through the point M (the intersection of the line $x = x_f$ and the rectifying line) (Figure 6), and the point N (coordinates x_w, x_w) (Figure 9). The stepwise procedure is started at point P (Figure 7) and carried through Figures 7, 6, 8, and 9 in turn, until the composition of the waste is reached with, in this case, the thirty-fifth step, and so the entire column contains $34\frac{1}{3}$ perfect plates. The cross-over from the rectifying line to the exhausting line occurs at the thirtieth step, and so the feed plate is the thirtieth plate from the top.

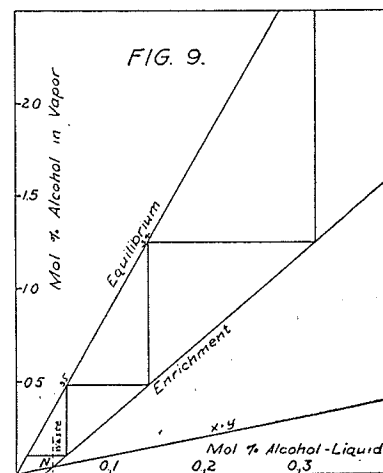
Most of the plates are in the range represented by Figure 7, and a small error in the equilibrium curve in this range introduces a relatively large error in the number of plates; but any method of calculation is subject to the same limitation.

For the sake of more open diagrams, the scale of the x -axis has been expanded to five times that of the y -axis, in Figures 8 and 9. This does not affect the construction or the result, except that it changes the angle of slope of the lines; thus, the $x = y$ line is no longer at 45 degrees.

For any binary combination, the equilibrium curve need be drawn only once, in ink perhaps; the enrichment lines and the steps may be drawn in lightly, with pencil, for any possible combination of overflow, and feed, product, and waste compositions.

If Lewis's results for the foregoing problem are multiplied by 0.8 to eliminate his assumption of 80 per cent plate efficiency, the results

are comparable, as in the table; Lewis's feed plate comes at a composition $x = 2.05$ mol per cent.



Number of Theoretical Plates

	Lewis	Authors
Above feed	31.0	29
Below feed	2.3	6.3
TOTAL	34.3	35.3

The accuracy of the results obtained by the graphical method is theoretically limited only by the error introduced by assuming constant molal overflow, whereas the accuracy of the Lewis method as applied to the foregoing example is limited, not only by the assumption given above, but also

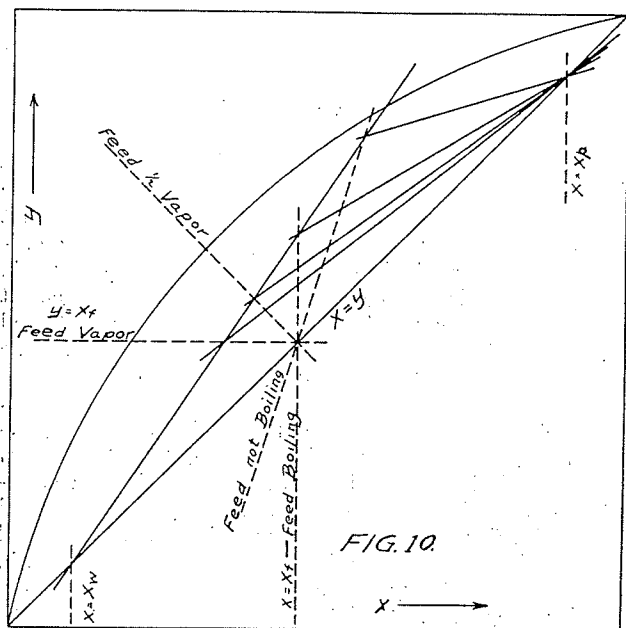


FIG. 10

by an additional assumption of differential changes from plate to plate. Therefore, any discrepancy between the results obtained by the two methods is a measure of the error introduced by the assumption of a continuous for a step-wise régime.

The agreement above the feed is very good, as was to be expected, since when the enrichment per plate is small Lewis's method, which is based on an assumption of differential enrichment, is most accurate. Below the feed the steps are very large, and the percentage error of the Lewis method is larger. In this particular case the differences nearly compensate, and the total number of plates is nearly the same in each case.

Partial Condenser

The effect of removing the restrictions imposed by the four assumptions made above will now be considered. The result of using a partial condenser in place of a total condenser is that the vapor rising from the top plate is weaker than the product. The enrichment equation is not affected so long as the composition of the product is known. Hence, with a partial condenser, instead of beginning the step corresponding to the first plate along the line $y = x_p$, it is begun at a line $y = y_1$, where y_1 is less than x_p , and must be computed from a knowledge of the design of the partial condenser, which is not in the province of this article.

Use of "Open Steam"

When the less volatile component of the mixture under consideration is water, the heat is often supplied to the base of the column by blowing in steam through a perforated pipe, and the waste is diluted by the steam so condensed. The latent heat of condensation of the entering steam will vaporize an equal weight of mixture (which is nearly all water), and the mols of steam used will equal the mols of vapor sent up the column, \bar{V} , which is in turn equal to $O + 1$. If x_w' is the composition of the diluted waste, and W' is the number of mols of the same, then

$$Wx_w' = W'x_w' \quad (19)$$

since the total amount of more volatile component lost in the waste is, in the case of closed steam, fixed as Wx_w .

It can be shown algebraically that in the case of open steam the exhausting line still passes through the point of intersection of the $x = y$ line and the line $x = x_w'$, and also crosses the x -axis at the point where $x = x_w'$. Therefore, it is only necessary to carry the steps, not only to where $x = x_w'$, but to the x -axis to allow for the effect of open steam.

Note—Open steam must be used where a closed coil would become fouled by the waste, but when used, the number of plates is increased (though very slightly in most cases) and the waste is diluted.

Feed Not at Boiling Point

If the feed is not wholly a liquid at its boiling point, the number of mols of vapor rising from the feed plate is not the same as that rising to it. If the feed is below the boiling point, the vapor rising to the feed plate will heat the feed to the boiling point by condensation, thereby increasing the overflow below the feed and decreasing the vapor above the feed by the number of mols condensed. If the feed is partly or wholly vapor, the vapor above the feed will be increased by the amount of vapor admitted, while the overflow below the feed will be less than $O + F$. In either case the effect on the diagram is to cause the locus of the intersection of the two enrichment lines to incline from the vertical.

Let q = the total heat needed to convert 1 mol of feed into saturated vapor, divided by the molal latent heat.

Then in the case of a liquid at the boiling point, $q = 1$.

In the case of a feed of wholly saturated vapor, $q = 0$.

If the feed is partly liquid and partly vapor, q is the fractional part which is liquid.

If the feed is below the boiling point, then q is greater than 1, and is equal to 1 plus the fractional part of a mol of vapor needed to raise one mol of feed to the boiling point.

In place of Equation 6 we have

$$\bar{O} = O + qF \quad (20)$$

Hence Equation 8 becomes

$$\bar{x}_n = \frac{(O - W + qF) -}{O + qF} y_{n+1} + \frac{Wx_w}{O + qF} \quad (21)$$

To find the locus of the intersection (for different values of O) of this enrichment line with that represented by Equation 1, eliminate O from Equations 1 and 21 and substitute for F its value as given by Equation 16. When this is done there results

$$qx - (q-1)y = x_f \quad (22)$$

This is the equation of a straight line. If $x = y$, then $x = y = x_f$. Hence this line always crosses the $x = y$ line at x_f . If $q = 1$, $x = x_f$. This is the result already given in Equation 17.

If $q = 0$ (feed a saturated vapor), $y = x_f$. In this case the locus is a horizontal line passing through $x = y = x_f$.

If $q > 1$, the slope is positive—i. e., up and to the right.

If $q < 1$, the slope is negative—up to the left.

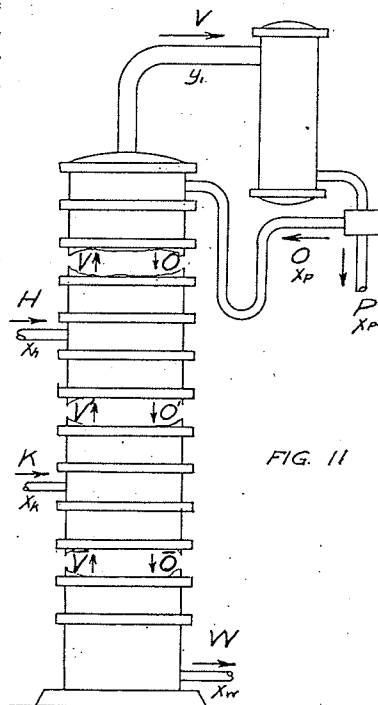


FIG. 11

These four cases are represented in Figure 10, where the number of mols of vapor rising to feed plate per mol of product is the same for all cases.

Variation on Molal Overflow

The molal overflow may not be constant in a column, for three reasons. The first cause may be a difference in the molal heats of vaporization of the two components. Allowance may be made for this by computing all quantities, not in mols, but in "latent heat units,"⁸ that is, in the quantities of liquid evaporated by any definite quantity of heat. Thus, if the liquids have heats of vaporization (per gram) of 969 and 305 calories, we may adopt as our base 969 calories and the latent heat units will be 969/969 and 969/305 grams of the two liquids, respectively. They will then be treated exactly as if they had molecular weights of 1 and 3.177, respectively. Since no chemical reaction takes place, the only reason for using mols at all is the fact that they correspond nearly to the more accurate "latent heat units;" if this correspondence does not hold there is no object in using them. If latent heat units are chosen, they must be used throughout—in the construction of the equilibrium curve as well as in expressing the compositions on each plate and of the feed, product, and waste.

The second reason why the overflow may vary is the change in boiling point of the liquids on the successive plates, and the third cause may be heat losses from the column. To allow for these effects rigorously would require the construction of a different enrichment line for every plate, and so would be tedious. However, the effects are usually small and tend to balance each other, so they rarely require consideration.

Note—The graphical methods of Ponchon⁹ and Savarit¹¹ are rigorously applicable to cases where the overflow varies, but these methods are rather complicated.

Two Feeds

Suppose it is desired to rectify in the same column two mixtures of the same two liquids but of different compositions. Let the mols of the two feeds (per mol of product) be H and K . Let x_h and x_k be the compositions of the mixtures. Similarly, let G and x_g be the amount and composition of the mixture that would be produced if the two feeds were mixed. Then

$$G = H + K \quad (23)$$

$$Gx_g = Hx_h + Kx_k \quad (24)$$

Let $x_h > x_k$ so that the "H" feed will naturally be put in higher up the column. The column is diagrammatically represented by Figure 11.

The original assumptions will be used. Through material balances it can be shown, by deriving the enrichment equations for the three parts of the column (above both feeds, between the feeds, and below both feeds), and determining the loci of their intersections by eliminating the overflow, that the enrichment lines for the top and bottom sections of the column cross the $x = y$ line at x_p and x_w , respectively, and intersect on the vertical line $x = x_g$; and that the enrichment line for the middle part of the column (between the two feed plates) must pass through two points—namely, the intersection of the upper enrichment line with the vertical line $x = x_h$ and the intersection of the lower enrichment line with the vertical line $x = x_k$. For a two-feed column, then, these rules follow:

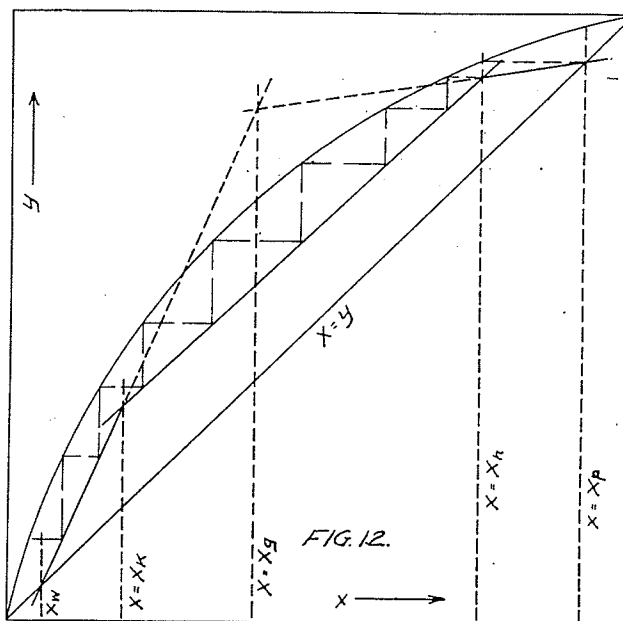
1—To construct the enrichment lines for a two-feed column, compute the composition that would result if the feeds were mixed. The enrichment lines for the ends of the column will be exactly the same as for a single-feed column that is fed with this mixture. The enrichment line for the middle of the column is found by joining the points where the enrichment lines for the ends intersect the lines $x = x_h$ and $x = x_k$, where x_h and x_k are the compositions of the two feeds.

2—If there are two feeds, each heated to boiling, each feed is to be admitted on the highest plate that has a composition lower than that feed.

These rules are illustrated in Figure 12. When the two feeds are very different in composition the column may function well when the feeds are put in at the proper points, though at the same overflow it would not function if the feeds were mixed.

If for any reason part of the liquid (not a third constituent) is withdrawn regularly from the column, the calculations are similar to those for two feeds, except that either H or K will be negative.

Mains¹⁴ has extended Lewis's method to the design of columns for the separation of mixtures such as furfural and water where the product, on cooling, forms two layers which can be separated in a continuous decanter and one of them returned to the column. This is a special case of a



two-feed column where the second feed is one of the layers formed in the decanter. If this second feed is not at the boiling point the enrichment line for that part of the column below the entrance of the decanted feed must be modified as described under the section "Feed Not at Boiling Point."

Acknowledgment

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¹⁴ *Chem. Met. Eng.*, 31, 307 (1924).

New Green Dye

The Dyestuffs Department of E. I. du Pont de Nemours & Company has just placed on the market a new chrome green, known as pontachrome green G, to take the place of pontachrome green GLO, which will be discontinued. It is bluer than pontachrome green GLO, but very similar in properties as well as in strength. Pontachrome green G can be applied as a straight color or can be used in combinations to produce browns, greens, or olives, and especially in mixtures to produce blacks that leave silk effects unstained.